

# A continental-weathering control on orbitally driven redox-nutrient cycling during Cretaceous Oceanic Anoxic Event 2

Simon W. Poulton<sup>1</sup>, Susann Henkel<sup>2</sup>, Christian März<sup>3</sup>, Hannah Urquhart<sup>3</sup>, Sascha Flögel<sup>4</sup>, Sabine Kasten<sup>2</sup>, Jaap S. Sinninghe Damsté<sup>5</sup>, and Thomas Wagner<sup>3</sup>

<sup>1</sup>School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

<sup>2</sup>Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

<sup>3</sup>School of Civil Engineering and Geosciences, Newcastle University, Drummond Building, Newcastle upon Tyne NE1 7RU, UK

<sup>4</sup>Helmholtz-Zentrum für Ozeanforschung Kiel (GEOMAR), Wischhofstrasse 1-3, 24148 Kiel, Germany

<sup>5</sup>NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, NL-1790 AB Den Burg (Texel), Netherlands

## ABSTRACT

The Cretaceous period (~145–65 m.y. ago) was characterized by intervals of enhanced organic carbon burial associated with increased primary production under greenhouse conditions. The global consequences of these perturbations, oceanic anoxic events (OAEs), lasted up to 1 m.y., but short-term nutrient and climatic controls on widespread anoxia are poorly understood. Here, we present a high-resolution reconstruction of oceanic redox and nutrient cycling as recorded in subtropical shelf sediments from Tarfaya, Morocco, spanning the initiation of OAE2. Iron-sulfur systematics and biomarker evidence demonstrate previously undescribed redox cyclicity on orbital time scales, from sulfidic to anoxic ferruginous (Fe-rich) water-column conditions. Bulk geochemical data and sulfur isotope modeling suggest that ferruginous conditions were not a consequence of nutrient or sulfate limitation, despite overall low sulfate concentrations in the proto-North Atlantic. Instead, fluctuations in the weathering influxes of sulfur and reactive iron, linked to a dynamic hydrological cycle, likely drove the redox cyclicity. Despite the potential for elevated phosphorus burial in association with Fe oxides under ferruginous conditions on the Tarfaya shelf, porewater sulfide generation drove extensive phosphorus recycling back to the water column, thus maintaining widespread open-ocean anoxia.

## INTRODUCTION

Major perturbations to the global Earth system occurred during the mid-Cretaceous, resulting in repetitive  $\delta^{13}\text{C}$  isotope excursions in organic carbon and carbonate linked to enhanced organic carbon burial (Jenkyns, 2010). Although the precise driving mechanisms varied for each of these perturbations, extreme greenhouse conditions were a common feature, leading to enhanced hydrological cycling and oceanic nutrient (phosphorus) inputs, particularly in equatorial regions (Wagner et al., 2013). Coupled with more restricted basinal conditions and limited ocean circulation, enhanced primary production promoted extensive carbon burial, ultimately resulting in the widespread development of anoxic oceanic conditions (Trabucho Alexandre et al., 2010; Monteiro et al., 2012).

Redox-sensitive element and biomarker records imply widespread euxinic (sulfidic) conditions during these oceanic anoxic events (OAEs), which intermittently extended from bottom waters into the lower photic zone (Sinninghe Damsté and Köster, 1998; Hetzel et al., 2009). There is evidence to suggest, however, that euxinic conditions fluctuated with ferruginous conditions on orbital time scales during OAE3 (Coniacian-Santonian) in the deep-sea proto-North Atlantic (März et al., 2008). The OAE3 black shales highlight a classic effect of redox fluctuations on phosphorus cycling

(März et al., 2008), whereby efficient recycling of phosphorus to the water column during euxinic periods (positive productivity feedback) contrasts with extensive burial of water-column phosphorus during ferruginous intervals (negative productivity feedback). If prevalent on a basinal or global scale, the development of ferruginous conditions with associated phosphorus burial would have had major implications for the persistence of elevated marine productivity and widespread anoxia. To date, however, no other studies have evaluated the potential for rapid redox cycling between euxinic and ferruginous conditions during any of the Cretaceous OAEs, and hence the prevalence, controls, and implications of such conditions are unknown.

To address this, we present a redox and nutrient reconstruction of an expanded shallow-marine black shale section of Cenomanian-Turonian age (OAE2) from the northwest African shelf at Tarfaya, Morocco (see the GSA Data Repository<sup>1</sup> for details of the geologic setting). A positive organic carbon isotope excursion of ~3‰ (Fig. 1) marks the onset of OAE2 (Tsikos et al., 2004), while distinct sedimentary

<sup>1</sup>GSA Data Repository item 2015320, methods and data, including geologic setting, model parameters and mineralogical analyses, is available online at [www.geosociety.org/pubs/ft2015.htm](http://www.geosociety.org/pubs/ft2015.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

cycles broadly relate to fluctuations in total organic carbon (TOC) content (Kuhnt et al., 2005). Obliquity forcing has recently been suggested to be the dominant driver of this cyclicity, with eccentricity forcing possibly being a secondary component in parts of the record (Meyers et al., 2012).

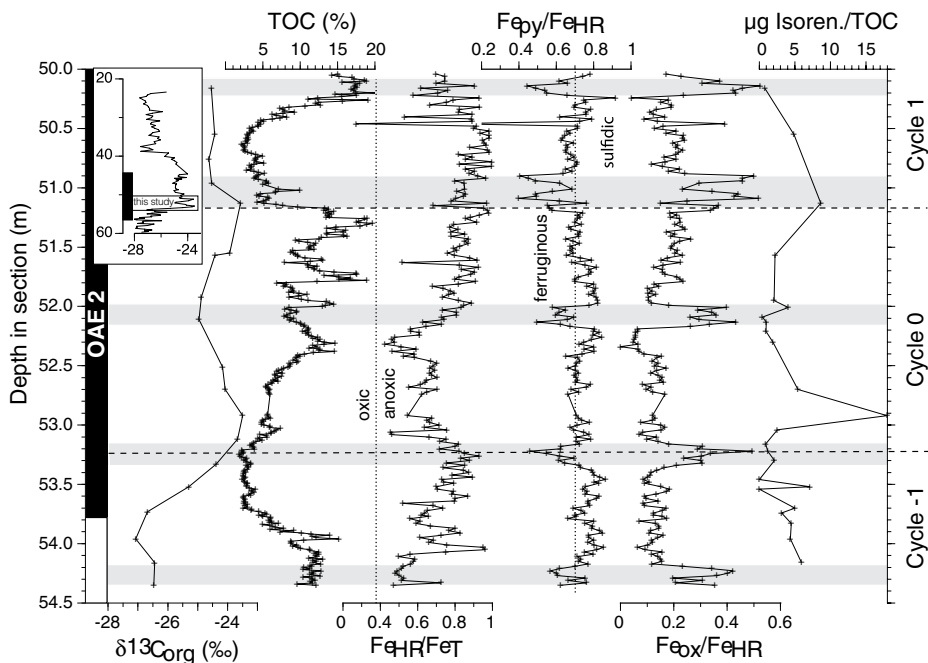
We focus on the onset of OAE2, as documented in records of centimeter-scale (millennial-scale) resolution from core S57 obtained from near the shelf basin center (Kuhnt et al., 2005). We utilize Fe-based redox proxies and molecular biomarkers to provide a detailed evaluation of oceanic redox conditions, and subsequently investigate controls on these conditions. Finally, we evaluate the behavior of phosphorus cycling during redox fluctuations on the Tarfaya shelf to provide new mechanistic insight into the maintenance of widespread anoxia during OAE2.

## METHODS

### Geochemical Analyses

Water-column redox conditions were evaluated using Fe speciation and molecular biomarker analyses. A “highly reactive” Fe fraction ( $\text{Fe}_{\text{HR}}$ ) was quantified via a calibrated extraction scheme which includes carbonate-associated Fe ( $\text{Fe}_{\text{carb}}$ ), ferric (oxyhydr)oxides ( $\text{Fe}_{\text{ox}}$ ), magnetite ( $\text{Fe}_{\text{mag}}$ ), and pyrite ( $\text{Fe}_{\text{py}}$ ) ( $\text{Fe}_{\text{HR}} = \text{Fe}_{\text{carb}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{py}}$ ; Poulton and Canfield, 2005). Modern and ancient sediments deposited from anoxic waters commonly have  $\text{Fe}_{\text{HR}}/\text{total Fe}$  ( $\text{Fe}_{\text{e}}$ ) ratios  $>0.38$ , in contrast to oxic depositional conditions, where ratios are consistently below this level (Poulton and Canfield, 2011). To provide further insight into the chemical nature of an anoxic water column, the extent to which the  $\text{Fe}_{\text{HR}}$  pool is pyritized distinguishes euxinic conditions ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.7$ ) from anoxic, ferruginous water-column conditions ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} < 0.7$ ).

Pyrite sulfur isotope compositions were determined on  $\text{Ag}_2\text{S}$  precipitates obtained through the Fe speciation techniques. Carbonate-associated sulfate (CAS) was determined according to refined techniques, and biomarkers for identifying photic zone euxinia (isorenieratane) were quantified by gas chromatography and gas chro-



**Figure 1.** Bulk geochemical, Fe speciation, and isorenieratane data for onset of Oceanic Anoxic Event 2 (OAE2), showing repetitive development of ferruginous conditions (gray shading). Sedimentary cycles are as defined by Kolonic et al. (2005). Vertical dashed lines represent boundary for distinguishing anoxic conditions ( $Fe_{HR}/Fe_T$  profile) and for distinguishing between euxinic and ferruginous conditions ( $Fe_{py}/Fe_{HR}$  profile). Inset graph shows interval studied in context of entirety of OAE2. TOC—total organic carbon; Isoren.—isorenieratane;  $Fe_{HR}$ —highly reactive Fe fraction;  $Fe_T$ —total Fe;  $Fe_{py}$ —pyrite;  $Fe_{ox}$ —ferric (oxyhydr)oxides.

matography–mass spectrometry (see the Data Repository for full details of samples, methods, and data).

### Sulfur Cycle Box Model

A standard sulfur-isotope box model (Adams et al., 2010) was used to estimate seawater sulfate concentrations in the proto–North Atlantic during the onset of OAE2 (see the Data Repository for full details of model parameters). Measured organic sulfur contents are ~6 times higher than pyrite sulfur contents on the Tarfaya shelf, while in the deeper proto–North Atlantic at Demerara Rise, organic sulfur burial was ~3 times higher than pyrite burial (Hetzl et al., 2009). Therefore, we include an organic sulfur component in the model and perform model runs where organic sulfur burial is set at 3 times (scenarios 1 and 2) and 6 times (scenario 3) the pyrite burial flux (Fig. 2). To maintain steady state after the addition of the organic sulfur burial flux term, we perform model runs with increased volcanic and/or weathering influxes of sulfur, consistent with the findings of previous studies (Adams et al., 2010; Blättler et al., 2011; Pogge von Strandmann et al., 2013).

## RESULTS AND DISCUSSION

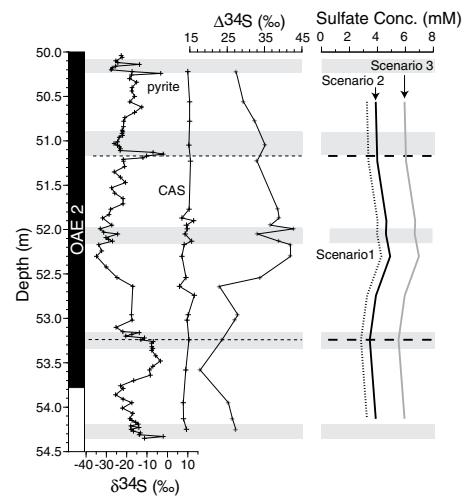
### Water-Column Redox Reconstruction

Elevated  $Fe_{HR}/Fe_T$  ratios are apparent throughout the analyzed core, suggesting persistent

bottom-water anoxia prior to, and during, the onset and initial maximum (as conventionally defined by the initial positive shift in carbon isotopes) of OAE2 (Fig. 1). Throughout the majority of the interval,  $Fe_{py}/Fe_{HR}$  ratios fall close to or above the 0.7 threshold, suggesting dominantly euxinic conditions. This is supported by the presence of the biomarker isorenieratane in all samples studied, which implies at least periodic incursions of sulfide into the lower photic zone, although the variability in concentration suggests that the temporal extent or intensity of photic zone euxinia may have fluctuated (Fig. 1). A pronounced feature is the cyclic development of ferruginous water-column conditions, where intervals of low  $Fe_{py}/Fe_{HR}$  (<0.7) correspond to enhanced preservation of ferric oxides ( $Fe_{ox}/Fe_{HR}$ ; Fig. 1). Ferruginous conditions occurred every half sedimentary cycle and are not related to changes in  $CaCO_3$  or TOC contents, arguing for a robust mechanism that operated on orbital frequencies.

### Controls on Redox Cycling

Fluctuations in nutrient levels as a potential driver of the transitions to ferruginous water-column conditions can be ruled out due to consistently high TOC (Fig. 1) and bio-essential trace metal availability (see the Data Repository). Instead, we first focus on the possibility that enhanced burial of seawater sulfate (as pyrite) during euxinic intervals controlled the



**Figure 2.** A: Sulfur (S) isotope profiles for pyrite and carbonate-associated sulfate (CAS), and fractions ( $\Delta^{34}S$ ) between CAS and pyrite. B: Estimated seawater sulfate concentrations based on modeling of S isotope data, showing no fluctuations associated with redox cyclicity. Scenario 1: Organic S burial flux set at 3 times pyrite burial flux; S weathering input flux increased by factor of 3.2 compared to modern (Blättler et al., 2011). Scenario 2: Organic S burial flux set at 3 times pyrite burial flux; volcanic S input flux increased by factor of 7.6 compared to modern (Adams et al., 2010). Scenario 3: Organic S burial flux set at 6 times pyrite burial flux; S weathering input flux increased by factor of 3.2 compared to modern (Blättler et al., 2011); volcanic S input flux increased by factor of 7.4 compared to modern (Adams et al., 2010). OAE2—Oceanic Anoxic Event 2; Conc.—concentration.

temporal extent of euxinia. The modern marine environment is delicately balanced with regard to the fluxes of sulfate and  $Fe_{HR}$  to the ocean, which are poised at a molar S: $Fe_{HR}$  ratio of ~1.8:1 (Poulton and Canfield, 2011). This ratio is slightly less than the 2:1 ratio of these elements in pyrite ( $FeS_2$ ; the main removal mechanism for sulfate from the ocean), suggesting that extensive depletion of seawater sulfate under euxinic conditions could potentially have led to an excess of  $Fe_{HR}$ , hence driving the water column ferruginous. This mechanism does not require complete removal of sulfate from the water column, but rather demands that rates of sulfide production under low sulfate conditions were overwhelmed by the influx of reactive Fe, thus restricting sulfide build-up to sediment porewaters (Meyers, 2007).

We evaluate this mechanism by considering sulfur isotope systematics through the analyzed section (Fig. 2). Our CAS analyses give a relatively constant seawater sulfate isotopic composition ( $\delta^{34}S$ ) of  $10\text{‰} \pm 2\text{‰}$  (Fig. 2). This value is significantly lower than contemporaneous values of ~19‰ determined from barite in Pacific sediments (Paytan et al., 2004) and CAS estimates that range from ~17‰ to 22‰ during

the early stages of OAE2 in relatively shallow-water settings from northern Europe (Owens et al., 2013). Our estimate is, however, closer to CAS values recorded immediately prior to OAE2 in sediments from Italy (14‰–18‰; Ohkouchi et al., 1999) and the Western Interior Seaway (10‰–13‰; Adams et al., 2010), suggesting significant spatial variability in seawater sulfate isotope compositions at this time. The sulfate isotope record has also been shown to vary temporally during OAE2, with isotopically light compositions in the run-up to the OAE being attributed to enhanced volcanism (Adams et al., 2010). Subsequently, transitions to more positive values (increasing by 2‰–7‰) toward the top of (or above) the OAE have been linked to extensive drawdown of seawater sulfate through enhanced pyrite burial (Ohkouchi et al., 1999; Adams et al., 2010; Owens et al., 2013). Despite this spatial and temporal variability, our high-resolution sulfur isotope analyses can be used to evaluate whether enhanced drawdown of seawater sulfate also operated on orbital time scales, thus driving the observed transitions to ferruginous conditions.

When incorporated into the sulfur isotope box model (Fig. 2), two robust conclusions can be drawn from our analyses. Firstly, consistent with studies from other areas (Ohkouchi et al., 1999; Paytan et al., 2004; Adams et al., 2010; Owens et al., 2013), seawater sulfate concentrations significantly lower than at present (28 mM) are indicated for the Tarfaya shelf. Indeed, our estimated range of ~3–7 mM (Fig. 2) is in close agreement with estimates of ~2–4 mM (Adams et al., 2010) and 7 mM (Owens et al., 2013) for the early stages of OAE2 in different oceanic basins. Secondly, a particularly important factor for our study is that reconstructed seawater sulfate concentrations are relatively constant throughout the analyzed interval (Fig. 2). Thus, the sulfur isotope record does not support enhanced drawdown of sulfate under euxinic conditions as a driver for the repeated development of ferruginous conditions, and an alternative mechanism must be sought.

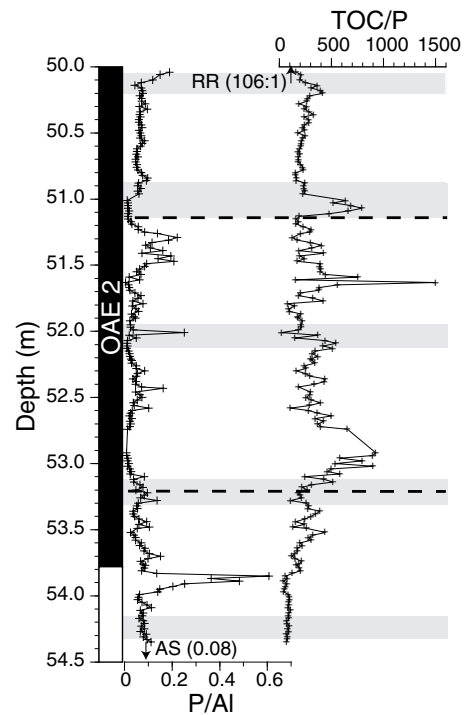
In this regard, we instead consider possible changes in the oceanic influx of sulfate and  $Fe_{HR}$ , which may have been driven by regular variability in continental weathering and runoff. A climate-driven control is supported by evidence for orbital-time-scale fluctuations in trade wind intensity and hydrological cycling, translating into alternations between more humid and drier periods (Wagner et al., 2013), and major element evidence for enhanced silicate weathering during some of the ferruginous intervals apparent in the Cretaceous (see the Data Repository). This increase in weathering intensity would have altered the proportional fluxes of sulfate and  $Fe_{HR}$  to the ocean on orbital time scales, the effects of which would have been particularly significant in an ocean characterized by

low sulfate. Sulfate is dominantly sourced from pyrite oxidation on land, which also releases  $Fe_{HR}$  (Fe released during pyrite oxidation ultimately forms Fe oxides), but enhanced silicate weathering would have provided an additional source of  $Fe_{HR}$  over sulfate, as Fe release from parent rocks increases with weathering intensity and continental runoff (Poulton and Raiswell, 2002). It is unclear whether a short-term weathering-induced increase in the relative flux of  $Fe_{HR}$  would have been sufficient, in isolation, to drive the proto-North Atlantic shelf ferruginous. In addition, however,  $Fe_{HR}$  minerals are dominantly (~85%) trapped in proximal settings such as floodplains and lagoons in the modern environment, whereas riverine dissolved sulfate is effectively mixed into the ocean (Poulton and Raiswell, 2002). Increased rates of continental runoff during the Cretaceous would have diminished this proximal  $Fe_{HR}$  sink by bypassing such settings, potentially resulting in a greatly enhanced flux of  $Fe_{HR}$  to the open shelf relative to sulfate. A proportional increase in the flux of  $Fe_{HR}$  over sulfate would increasingly restrict sulfidic conditions to the sediments (Meyers, 2007), ultimately promoting the development of ferruginous conditions.

#### Phosphorus Cycling and Implications for the Maintenance of Widespread Anoxia

Euxinic-ferruginous redox cycling has major implications for phosphorus bioavailability, as demonstrated for black shales deposited during OAE3 at Demerara Rise (März et al., 2008), with the possibility of extensive phosphorus burial under ferruginous conditions, in contrast to effective phosphorus recycling to the water column under euxinic conditions. This possibility is important to evaluate at Tarfaya, because extensive phosphorus burial under ferruginous conditions would have limited marine productivity and hence call into question the role of persistently elevated phosphorus in maintaining anoxia during OAE2 (cf. Mort et al., 2007). Consistent with a rise in reactive phosphorus burial at the onset of OAE2 observed in a number of global localities (Mort et al., 2007), P/Al ratios are significantly enhanced at this point in the Tarfaya core (Fig. 3). In contrast, the remainder of the analyzed interval is characterized by P/Al ratios at or below average shale, with no evidence for enhanced burial under ferruginous conditions. Building upon this observation, molar TOC/P ratios are consistently above the Redfield ratio after the onset of OAE2, suggesting effective recycling of phosphorus to the water column (Van Cappellen and Ingall, 1994) during both euxinic and ferruginous intervals on the Tarfaya shelf.

To explain these observations we suggest that although phosphorus was likely initially sequestered in the sediment during ferruginous intervals, in association with either organic mat-



**Figure 3.** P/Al and molar total organic carbon (TOC)/P profiles for Oceanic Anoxic Event 2 (OAE2) sediments at site S57, Tarfaya, showing extensive release of phosphorus under euxinic and ferruginous conditions. Arrows represent average shale (AS, P/Al profile) and the Redfield ratio of 106:1 (TOC/P profile).

ter or Fe (oxyhydr)oxide minerals (Fig. 1), sulfide production in sediment porewaters on the Tarfaya shelf was sufficient to remobilize this sequestered phosphorus back into the water column, via either sulfide-promoted reduction of Fe oxides or preferential release of phosphorus from organic matter during bacterial sulfate reduction (Van Cappellen and Ingall, 1994). This interpretation is supported by significant pyritization of the  $Fe_{HR}$  pool throughout ferruginous intervals on the Tarfaya shelf (Fig. 1), suggesting abundant sulfide availability during early diagenesis, which would also have preserved  $Fe_{HR}$  enrichments in the sediment (Scholz et al., 2014). In fact, the presence of isorenieratane and the occasional occurrence of  $Fe_{py}/Fe_{HR}$  ratios >0.7 during ferruginous intervals suggest that rates of bacterial sulfate reduction may have been sufficient to result in short-lived episodes of water-column euxinia punctuating ferruginous intervals (Fig. 1), further promoting phosphorus recycling within the water column itself.

#### CONCLUSIONS

Our data provide the first evidence for distinct redox cyclicity between euxinic and ferruginous water-column conditions during OAE2, apparently driven by orbital fluctuations in continental hydrology and weathering. This redox cyclicity occurs both during and prior to the onset of OAE2, and has also been observed in

a deeper-water section during OAE3 (März et al., 2008), suggesting that such conditions were likely a pervasive feature of anoxic water-column conditions in the Cretaceous greenhouse ocean. It remains to be seen, however, just how temporally and spatially expansive such conditions were. Nevertheless, our observation of extensive remobilization of phosphorus from the Tarfaya shelf under ferruginous conditions highlights an efficient mechanism by which elevated primary productivity and anoxia could have been sustained in the open ocean. It is equally possible that these redox-nutrient feedbacks may have operated as a major control on the spatial and temporal extent of ocean anoxia during other periods of Earth history.

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